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For and on behalf of RWS Group Ltd

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**Natural paper having good printability**

[0001] The present application relates to a natural paper having good printability. The present application furthermore relates to the provision of a process for the production of natural papers having good printability.

5 [0002] In the paper industry, attempts are constantly being made to improve the printability of papers. This applies in particular to papers which are used in offset printing and to papers for the new digital print media, such as, for example, inkjet papers or papers for digital printers. In the case of the papers which are used for said printing processes, it is possible in principle to distinguish between  
10 two classes of papers: the natural papers and the coated papers. In the case of the coated papers, at least one coating which usually consists of pigments, binders and additives is applied to that side of the paper on which printing is to be effected. For improving the printability, a plurality of coats, such as, for example, two or three coats, can also be applied to the coated papers. This improves the  
15 printability as a function of the coverage of the web of the raw paper, i.e. the more coating applied, the better is the printability.

[0003] The applied coatings can be divided into two classes, namely the glossy and the matt coatings. They differ in their composition and in the subsequent processing steps in the production of the coated papers. A surface treatment by means of a calender or a smoothing unit after application of the coating  
20 will be mentioned in particular here. A disadvantage here is that the impression, i.e. the appearance and the feel, i.e. the haptic properties, of the paper is adversely affected by the applied coatings.

[0004] Natural papers do not have these disadvantages. Since they have  
25 no coating with the high coat weights of the coated papers, the original character of the paper is retained. In particular, the stiffness and the surface structure of the natural paper are not changed or not significantly changed. This leads to a pleas-

ant feel on touching the papers (pleasant haptic properties) and a pleasant visual appearance of these papers. For this reason, they are used for high-quality applications, such as, for example, office correspondence or demanding catalogs, brochures and books, especially those which are artistically designed. The quality of  
5 the print on natural papers is, however, poorer than on coated papers. The surface contour of the natural paper is recognizable in the print.

[0005] Owing to the fiber structure of the natural papers, the surface of which, expressed simply, consists of peaks and valleys, the printing ink is accepted to different extents in the printing process. Particularly in the case of multi-  
10 color prints, this has a disadvantageous effect since superposition of the individual printing inks results here and the surface structure of the natural paper is thus particularly visible in the print.

[0006] There has been no lack of attempts to combine both the visual impression and the haptic properties of a natural paper with the good printability of a  
15 coated paper.

[0007] EP 0 648 894 proposes providing a cardboard with a coating which has a coat weight of  $1 - 5 \text{ g/m}^2$  and consists of a pigment having an oil absorptivity of at least  $80 \text{ g/100 g}$  of pigment and a binder. A disadvantage is that the composition described in EP 0 648 894 can be used only on boxboards having high  
20 weight, which preferably have a basis weight of at least  $180 \text{ g/m}^2$ .

[0008] In US 6,387,213 the printability of a paper is improved by applying a composition which contains a hollow plastic pigment in a proportion of 30-60% by weight, based on the dry weight of the coating. Furthermore, the formulation contains a binder in a proportion of 40 – 70% by weight based on the dry weight in the  
25 formulation, which binder is a modified starch having a high molecular weight. The formulation should preferably be applied as a contour coat to the paper substrate. The high costs of the coating, which are due to the hollow plastic pigment and the modified starch having a high molecular weight, are disadvantageous here.

[0009] EP 1 146 171 adopts another approach for improving the printability of a paper. A top coat which contains a pigment and a rheology-modifying/binder component is applied to a paper substrate which has a surface roughness of less than 6  $\mu\text{m}$  and a surface gloss of 5 – 80%. Here, it is preferable if the top coat is  
5 applied as a single coat having a coat thickness which preferably corresponds to the size of a pigment particle. A disadvantage of the paper presented in EP 1 146 171 is that the paper substrate must have a defined surface roughness of less than 6  $\mu\text{m}$  and that the top coat must be applied to the substrate in a coat thickness which corresponds to the size of the pigments.

10 [0010] The subsequently published European Patent Application 03 000 835.3 describes how it is possible to produce a patterned paper which is dyed with nonuniform intensity. A mixture which contains at least one surfactant and at least one pigment is applied nonuniformly to a paper, i.e. not over the entire surface, a latent image or pattern forming. In a subsequent step, the paper is nonuniformly  
15 dyed by application of a dye solution and then dried. What is essential here is that the mixture of surfactant and pigment is applied to the paper not uniformly but only in the areas where a pattern is to be subsequently recognizable. The changed coloring may be both a more intense and a less intense coloring in comparison with the untreated surface of the paper. European Patent Application 03 000  
20 835.3 does not disclose that the mixture of surfactant and pigment is applied to a paper substrate over the entire surface.

[0011] The object of the present invention is to provide a paper which combines the good printability of coated papers with the haptic properties and the visual impression of the natural papers. In particular, the papers should be improved  
25 compared with papers produced to date in such a way that very good printability by a very wide range of printing processes can be achieved, in particular by offset printing, digital printing and inkjet printing. Otherwise, the properties peculiar to the natural papers should be retained.

[0012] The technical object of the present invention is achieved by a paper comprising:

a) a paper substrate and

b) a preparation applied to at least one side of the paper substrate over the entire  
5 surface and containing a surfactant and at least one pigment having a particle diameter of from 1 to 500 nm, the preparation containing a binder in a ratio to the pigment of not more than 5 parts by weight of binder : 100 parts by weight of pigment (based in each case on the solids content).

[0013] It was found that the printability in the customary printing processes  
10 is improved if such a preparation penetrates into the paper substrate, the haptic properties and the visual impression of the natural paper simultaneously being retained. The preparation completely or virtually completely encloses mainly the fibers localized at the surface of the paper substrate.

[0014] An advantage is that the natural paper of the present invention can  
15 be produced on units which are customary in the paper industry, so that no additional production units are required. It is furthermore advantageous that the natural paper of the present invention can be recycled so that it can be disintegrated in customary plants, such as, for example a pulper, and can be used again for the further production of paper.

20 [0015] In the context of this invention, the term paper is to be understood as meaning the finished, printable paper. It can be present both as continuous product/product on reels and as product cut to size. The paper comprises a paper substrate as support material and a preparation applied to at least one side of the paper substrate. The coating is a layer which is optionally applied to the side of  
25 the paper substrate on which the preparation is present. If coat weights are stated they relate to the applied mass per unit area after conditioning to constant weight at 110°C (absolutely dry). Preferred embodiments will be discussed below.

[0016] In a preferred embodiment, the preparation can be applied to both sides of the paper substrate, i.e. to the top and the bottom of the paper substrate, over the entire surface.

[0017] The preparation may have an overall anionic, cationic or neutral  
5 charge.

[0018] In a preferred embodiment, the preparation has a coat weight of 0.5 – 20 g/m<sup>2</sup> (absolutely dry) per side. Preferably 1 – 15 g/m<sup>2</sup>, more preferably 2 – 10 g/m<sup>2</sup> and particularly preferably 3 – 7 g/m<sup>2</sup> of preparation are present on at least one side of the paper substrate, over the entire surface.

10 [0019] Preferably 0.05 – 2.5 g/m<sup>2</sup> (absolutely dry) of surfactant are present per side in the preparation. A preferred embodiment comprises 0.1 – 2.0 g/m<sup>2</sup>, more preferably 0.2 – 1.5 g/m<sup>2</sup> and most preferably 0.3 – 0.7 g/m<sup>2</sup> of surfactant in the preparation.

[0020] The surfactant can preferably be an anionic, cationic, nonionic or  
15 amphoteric surfactant.

[0021] For example, suitable surfactants can be selected from (1) hydrophilic polydialkylsiloxanes, (2) polyalkylene glycol, (3) polypropylene oxide/polyethylene oxide copolymers, (4) fatty acid ester-modified compounds of phosphate, sorbitan, glycerol, polyethylene glycol, sulfosuccinic acids, sulfonic  
20 acid or alkylamine, (5) polyoxyalkylene-modified compounds of sorbitan esters, fatty amines, alkanolamides, castor oil, fatty acid, fatty alcohol, (6) quaternary alcohol sulfate compounds, (7) fatty imidazolines, (8) polyether-modified trisiloxanes and (9) mixtures thereof.

[0022] Specific examples of water-soluble or alcohol-soluble surfactants  
25 from the abovementioned classes of substances are, for example, (1) poly(oxyalkylene) modifications of (a) sorbitan esters (e.g. Alkamuls PSML-4



(poly(oxyethylene)sorbitan monolaurate), Alkamuls PSMO-20 (poly(oxyethylene)sorbitan monooleate), Alkamuls PSTO-20 (poly(oxyethylene)sorbitan trioleate), Alkaril Chemicals); (b) fatty amines (e.g. Alkaminox T-2, T-5 (tallow aminoxyethylate), Alkaminox SO-5(soya bean aminoxyethylate), Alkaril Chemicals, 5 (Icomeen T-2, Icomeen T-15, ICI Chemicals); (c) castor oil (e.g. Alkasurf CO-10, Alkasurf CO-25B (castor oil oxyethylates), Alkaril Chemicals); (d) alkanolamide (e.g. Alkamide C-2, C-5 (coconut oil alkanolamide oxyethylates), Alkaril Chemicals); (e) fatty acids (e.g. Alkasurf 075-9, Alkasurf 0-10, Alkasurf 0-14 (oleic acid oxyethylates), Alkasurf L-14 (lauric acid oxyethylates), Alkasurf P-7 (palmitic acid oxyethylates) Alkaril Chemicals); (f) fatty acid alcohol (e.g. Alkasurf LAN-1, LAN-3, 10 Alksasurf TDA-6, Alkasurf SA-2, (linear alcohol oxyethylates), Alkasurf NP-1, NP-11, Rexol 130 (nonylphenol oxyethylates), Alkasurf OP-1, OP-12 (octylphenol oxyethylates), Alkasurf LA-EP-15, Alkasurf LA-EP-25, Alkasurf LA-EP-65 (linear alcohol oxyalkylates)); (2) hydrophilic poly(dimethylsiloxanes) such as, for example, 15 (a) poly(dimethylsiloxane) provided with a monocarbinol terminal group (PS558, Petrarch Systems Inc.) and poly(dimethylsiloxane) provided dicarbonol terminal group (PS555, PS556, Petrarch Systems Inc.); (b) poly(dimethylsiloxane)-b-poly(methylsiloxanalkylene oxide) copolymers (PS 073, PS 072, PS 071, Petrarch Systems Inc.), Alkasil HEP 182-280, Alkasil HEP 148-330 (Alkaril Chemicals), 20 nonhydrolyzable copolymers containing Si-C-bonds; (c) poly(dimethylsiloxane)-b-poly(propylene oxide)-b-poly(ethylene oxide) copolymers (Alkasil NEP 73-70, Alkaril Chemicals) a hydrolyzable copolymer containing Si-O-C-bonds; (d) polyquaternary poly(dimethylsiloxane) copolymers (which can be obtained by the addition reaction of an  $\alpha,\omega$ -hydrogenpolysiloxane with epoxides containing olefinic bonds and subsequent reaction of a product with a diamine); (3) 25 fatty imidazolines and their derivatives, such as for example, (a) Alkazine-O (oleyl derivative); (b) Alkazine TO (tall oil derivatives); (c) Alkateric 2C1B (dicarboxylic acid cocosimidazoline sodium salt) Alkaril Chemicals; (d) Arzoline-4; (e) Arzoline-215, Baker Chemicals; (4) fatty acid esters of (a) phosphates (e.g. Alkaphos B6-56A, Alkaril Chemicals); (b) sorbitan (e.g. Alkamuls STO (sorbitan trioleate), Alka- 30 muls SML (sorbitan monolaurate), Alkamuls SMO (sorbitan monooleate), Alkaril Chemicals); (c) glycerol compounds (e.g. Alkamuls GMO-45LG (glyceryl monooleate), Alkamuls GDO (glyceryl dioleate), Alkamuls GTO (glyceryl trioleate); (d)

poly(ethylene glycols) (Alkamuls 600 DO (dioleate), Alkamuls 400-ML (mono-laurate), Alkamuls 600 MO (monooleate), Alkamuls 600 DL (dilaurate), Alkamuls 600 DT (ditallow), Alkaril Chemicals); (e) sulfosuccinic acid (e.g. Alkasurf SS-O-75 (sodium dioctylsulfosuccinate), Alkasurf SS-DA4-HE (oxyethylated alcohol sulfosuccinate), Alkasurf SS-L7DE (sodium sulfosuccinate ester of lauric acid diethanolamide), Alkasurf SS-L-HE (sodium laurylsulfosuccinate), Alkaril Chemicals); (f) sulfonic acid (e.g. Alkasurf CA (calcium dodecylbenzenesulfonate), Alkasurf IPAM (isopropylamine dodecylbenzenesulfonate), Alkaril Chemicals); (g) alkylamines (e.g. Alkamide SDO (soya bean diethanolamide), Alkamide CDE (coconut diethanolamide), Alkamide 2104 (coconut fatty acid diethanolamide), Alkamide CMA (coconut monoethanolamide), Alkamide L9DE (lauryl diethanolamide), Alkamide L7Me (lauryl monoethanolamide), Alkamide L1PA (lauryl monoisopropylamide), Alkaril Chemicals); (5) quaternary compounds, such as, for example, (a) non-polymeric quaternary ammonium ethosulfate (e.g. Finquat CT, Cordex T-172, Finetex Corporation); (b) quaternary dialkyldimethylmethosulfate (e.g. Alkaquat DHTS (hydrogenated tallow)); (c) alkoxylated quaternary di-fatty methosulfate (e.g. Alkasurf DAET (tallow derivative)); (d) quaternary fatty idazoline methosulfate (e.g. Alkaquat T (tallow derivatives), Alkaril Chemicals); (6) water-soluble copolymers of lipophilic poly(propylene oxide) with hydrophilic poly(ethylene oxide) such as, for example, (a) methanol-soluble Tetronic 150R1, Pluronic L-101, Tetronic 902, Tetronic 25R2 (BASF Corporation), Alkatronic EGE-1 (Alkaril Chemicals); (b) water-soluble Tetronic 908, 50R8, 25R8, 904, 90R4, Pluronic F-77, all from BASF Corporation, and Alkatronic EGE 25-2 and PGP 33-8 from Alkaril Chemicals; (7) poly(alkylene glycol) and its derivatives, such as, for example (a) polypropylene glycol (Alkapol PPG 425, Alkapol PPG-4000, Alkaril Chemicals); (b) poly(propylene glycol dimethacrylate), poly(ethylene glycol diacrylate), poly(ethylene glycol dimethacrylate), poly(ethylene glycol monomethyl ether), poly(ethylene glycol dimethyl ether), poly(ethylene glycol diglycidyl ether) (all from Polysciences); (c) poly(1,4-oxybutylene glycol) (Scientific Polymer Products) and the like.



[0023] Preferred surfactants include linear alcohol oxyethylates (e.g. Alkasurf LA-EP-65, LA-EP-25 and LA-EP-15 obtainable from Alkaril Chemicals), nonylphenol oxyethylates (e.g. Alkasurf NP-11 obtainable from Alkaril Chemicals and Rexol 130 obtainable from Hart Chemicals), octylphenol oxyethylates (e.g. Alkasurf OP-12 obtainable from Alkaril Chemicals), oleic acid oxyethylates (e.g. Alkasurf O-14 obtainable from Alkaril Chemicals), poly(dimethylsiloxane)-b-poly(propylene oxide)-b-poly(ethylene oxide) copolymers (e.g. Alkasil NEP 73-70 obtainable from Alkaril Chemicals), castor oil ethoxylates (e.g. Alkasurf CO25B obtainable from Alkaril Chemicals), cocosimidazolinedicarboxylic acid sodium salts (e.g. Alkateric 2C1B obtainable from Alkaril Chemicals) and coconut fatty acid diethanolamide (e.g. Alkamid S104 obtainable from Alkaril Chemicals). The Alkasurf surfactants are advantageously biodegradable.

[0024] Further preferred surfactants are fatty alcohols modified with ethylene oxide/propylene oxide, and modified fatty alcohol polyglycol ethers, such as, for example, Hydropalat® 120 XP (obtainable from Cognis/Henkel)

[0025] Preferably  $0.1 - 19.5 \text{ g/m}^2$  (absolutely dry) of pigment are present in the preparation. Preferably from  $0.2$  to  $19.3 \text{ g/m}^2$ , more preferably from  $0.3$  to  $18.5 \text{ g/m}^2$ , particularly preferably from  $0.4$  to  $18 \text{ g/m}^2$  and most preferably from  $0.45$  to  $17.5 \text{ g/m}^2$  of pigment are present in the preparation. The pigment can preferably have an overall cationic and/or anionic and/or nonionic charge. In the context of this invention, anionic pigments are those pigments in which the surface of the pigment has an overall anionic charge. Cationic pigments are those pigments in which the surface of the pigment has an overall cationic charge. Nonionic pigments are those pigments in which the surface of the pigments has an overall neutral or substantially neutral charge.

[0026] The pigment is preferably an oxide and/or mixed oxide of a metal. However, it may also be the oxide and/or mixed oxide of a semi-metal/semiconductor.

[0027] The pigments used in the preparation preferably have a large specific BET surface area of, preferably, from 50 to 800 m<sup>2</sup>/g and more preferably from 100 to 400 m<sup>2</sup>/g. The pigment particles themselves have a diameter of 1 – 500 nm, preferably 10 – 100 nm and more preferably 20 – 70 nm.

5 [0028] The pigments can preferably be selected from the group consisting of oxides of metals or semimetals, such as, for example, silicon, magnesium, calcium, aluminum, zinc, chromium, iron, copper, tin or lead. Preferred pigments are silicas, gibbsite, bayerite, nordstrandite, boehmite, pseudoboehmite, diaspore, aluminas, preferably corundum, aluminum hydroxide, magnesium silicate, basic  
10 magnesium carbonate, titanium dioxide, tin oxide, aluminum silicate, calcium carbonate, talc, clay, hydrotalcite, silica, colloidal silica, precipitated silica, inorganic substances, such as, for example, diatomite, organic substances, such as, for example, resin-like pigments comprising melamine/formaldehyde resins, urea/formaldehyde resins, ethylene resins, styrene resins, acrylate resins or combinations thereof.  
15

[0029] Colloidal suspensions of SiO<sub>2</sub> particles, which are preferably non porous SiO<sub>2</sub> particles can also be used as pigment. The suspension can have an anionic or cationic charge. Here, the particle size of the SiO<sub>2</sub> particles can vary from 1 to 100 nm, the particle size preferably being from 10 to 50 nm. The Cartacoat<sup>®</sup> K grades from Clariant, in particular Cartacoat<sup>®</sup> 301A liquid, Cartacoat<sup>®</sup> 302A liquid, Cartacoat<sup>®</sup> 302C liquid and Cartacoat<sup>®</sup> 303A liquid, may be mentioned by way of example for this class of pigments. Alternatively, anionic or cationic colloidal silica, which is sold under the trade name Ludox<sup>®</sup> CL or Ludox<sup>®</sup> TMA by Grace-Davison, can be used.  
20

25 [0030] Preferably at least one additive may be present in the preparation. Additives which may be used are those which are familiar to the person skilled in the art, such as, for example, rheology modifiers, viscosity regulators (thickeners), dyes or brighteners. If a viscosity regulator is used, it is preferable to use crosslinked modified polyacrylates, such as, for example, Cartacoat<sup>®</sup> MS liquid,

obtainable from Clariant. According to the invention, however, the preparation contains a binder in a ratio of binders to pigment (based in each case on solids content) of not more than 5 : 100, preferably not more than 3 : 100, particularly preferably not more than 2 : 100, in order to obtain the haptic properties of natural  
5 paper.

[0031] The binders used are preferably those which do not have a crosslinking effect, so that no solidification of the applied preparation layer occurs. In the strict sense, according to the invention no "binder" is used in the preparation but preferably thickeners or viscosity regulators, which, however, can also be used  
10 as binders in papermaking, such as, for example, cellulose (types), such as carboxymethylcellulose (CMC), are used for adjusting the flowability of the preparation. The thickeners are, however, used in amounts which are so small that they do not act as binders in the preparation, i.e. do not bind the pigments to one another and/or the pigments to the paper substrate, but merely adjust the viscosity  
15 and flowability of the preparation to be applied to a desired value. Such thickeners or viscosity regulators are generally known to the person skilled in the art in the area of papermaking. According to the invention, the thickeners do not have to meet any particular requirement. The amount of the thickener used is in the customary range in which such agents are used and depends on the properties of the  
20 thickener used.

[0032] According to the invention, binder for the purpose of binding the pigments to one another and to the paper substrate is not used in the preparation. Even if a thickener which is also suitable as a binder is used, it is present only in amounts which do not permit binding as described above. Such a preparation  
25 without "binder" used for the purpose of binding improves the printability of the paper substrate without substantially changing the haptic properties, so that said properties substantially correspond to those of natural paper.

[0033] The paper substrate preferably contains a filler. It is preferable if the filler has a cavity volume. The cavity volume of the filler can preferably be measured by the oil number of the filler, according to DIN EN ISO 787-5.

[0034] According to DIN EN ISO 787-5, the filler preferably has an oil number of 10 – 150 g/100 g of filler, more preferably of 30 – 80 g/100 g of filler and particularly preferably of 30 – 70 g/100 g of filler.

[0035] The filler can preferably be selected from the group consisting of chalk, precipitated chalk, clay, talc, calcined clay, alumina, aluminum hydroxide, gypsum, hydrated alumina, silica, silicic acid, diatomaceous earth, titanium dioxide, and mixtures thereof. The filler may furthermore preferably have an overall anionic or an overall cationic charge.

[0036] The proportion of filler in the paper substrate is preferably 3 – 30% by weight, based on the total weight of the paper substrate after conditioning at a constant weight at 110°C (absolutely dry). Preferably, the proportion of filler is 5 – 25% by weight, more preferably 7 – 20% by weight, particularly preferably 9 – 18% by weight and most preferably 10 – 15% by weight.

[0037] The paper substrate can preferably contain at least one additive. Preferred additives are wet strength agents, starches, antifoams, retention aids, brighteners, dyes and mixtures thereof. In a preferred embodiment, the paper substrate contains a proportion of wet strength agents which makes it possible to moisten the paper substrate again in the subsequent processing steps without the strength being reduced by water absorption to such an extent that the paper web tears during subsequent processing steps.

[0038] The paper substrate may contain all fibers customary for the person skilled in the art, such as, for example, chemical pulp or groundwood. Preferably, the paper substrate contains a mixture of long-fiber and short-fiber chemical pulps.

[0039] The paper preferably has a basis weight, varied according to ISO 536, of from 40 to 400 g/m<sup>2</sup>. The basis weight is preferably from 60 to 300 g/m<sup>2</sup>, more preferably from 70 to 280 g/m<sup>2</sup> and most preferably from 80 to 250 g/m<sup>2</sup>.

[0040] The preparation can be applied at least to one side of the paper substrate online, i.e. within the paper machine, to the paper substrate. Preferred coating units are the size press coating units similar to the size press, the film press, the billblade, the curtain coater, the airbrush, the blade, doctor blade coating and spray coating.

[0041] It is however also possible to apply the preparation at least to one side of the paper substrate in a finishing step downstream of the production of the paper substrate. This can be effected by means of coating units which are familiar to the person skilled in the art, such as, for example, by means of a size press, a coating unit similar to the size press, a film press, a blade, an airbrush, a doctor blade, a curtain coater, a spray coater or a reverse gravure coating unit.

[0042] Unexpectedly, the preparation improves the printability of the paper substrate without having a substantial or detectable disadvantageous influence on the optical or the haptic properties of the paper substrate. The paper substrate retains or virtually retains the visual and haptic impression of an untreated natural paper. The preparation penetrates over the entire surface and uniformly into the surface of the paper substrate and thereby unexpectedly prevents the irregularity of a subsequently applied print, which irregularity is otherwise caused by the peaks and valleys of the paper surface. Thus, for example, in offset printing, the ink application is uniform. An indication of this is the so-called mottling of the printed paper. The mottling indicates how homogeneous the printout in offset printing on the paper is. With a paper of the present invention, the homogeneity of the offset print is comparable with the homogeneity of the offset print on a coated paper. Furthermore, the paper of the present invention has a stiffness and a volume which are comparable with untreated and uncoated papers.



[0043] In a further embodiment, at least one further coating may be present on the preparation on the same side of the paper substrate on which the preparation is applied.

[0044] The coating preferably contains at least one pigment and at least one  
5 binder.

[0045] In a preferred embodiment, the applied pigment has a particle diameter of from 1 to 500 nm and can preferably be selected from the group consisting of oxide and/or mixed oxide of a metal, oxide and/or oxide of a semi-metal/semiconductor and mixtures thereof. More preferably, it is possible to use  
10 all pigments which can also be used as a pigment in the preparation.

[0046] The coating can preferably contain at least one further additive. Additives which may be used are all additives which are familiar to the person skilled in the art, such as, for example, binders, viscosity regulators (thickeners), brighteners, antifoams, dyes, dispersants and surfactants. Surfactants which may be  
15 used are all surfactants which are familiar to the person skilled in the art, and preferably the surfactants which are used in the preparation. Furthermore, it is possible to use all viscosity regulators which can also be used in the preparation. The coating preferably has a coat weight of  $0.5 - 20 \text{ g/m}^2$  (absolutely dry) per side. Preferably, the coat weight of the coating is  $2 - 15 \text{ g/m}^2$ , more preferably  $3 - 12$   
20  $\text{g/m}^2$  and most preferably  $3 - 10 \text{ g/m}^2$ . The coat weight of the coating is preferably such that the surface of the paper substrate on which the preparation is present is homogeneously wetted by the coating.

[0047] The coating can be applied to both sides of the paper substrate if a preparation is present on both sides of the paper substrate. However, if a preparation is present on both sides of the paper substrate, it is also possible for the  
25 coating to be applied on the preparation only on one side of the paper substrate.

[0048] The coating may have an overall anionic, cationic or netural charge. Preferably, the coating has an overall anionic charge if the preparation has an overall cationic charge, or the coating preferably has an overall cationic charge if the preparation has an overall anionic charge.

5 [0049] The coating can be applied using any coating unit which is familiar to the person skilled in the art. Furthermore, the coating can be applied within the paper machine (online), i.e. during the production of the paper substrate. However, it is just as possible to apply the coating after production of the paper substrate in a subsequent processing step. Suitable coating units are, for example,  
10 the size press, coating units similar to the size press, the film press, the blade coater, the airbrush, the doctor blade, the curtain coater and the spray coater.

[0050] All abovementioned papers (with or without the coating) can furthermore be subjected to aftertreatment steps. Thus, the surface of the paper can be further calendered. This can be effected by a smoothing unit, a matt calender, a  
15 calender or a brush calender. Those processes in which the smoothness of the paper is increased without the volume of the paper being substantially reduced by this step are advantageous. Alternatively, the surface contour of the paper can be changed by an embossing step. For example, an embossing calender is suitable for this purpose. The surface structure can be changed on both sides of the paper  
20 or only on one side of the paper, which is preferably the side on which the preparation is present.

[0051] All abovementioned papers can be used as a print medium in printing processes which are familiar to the person skilled in the art. It is preferable if the printing process is selected from the printing processes consisting of offset print-  
25 ing, digital printing, inkjet printing, gravure printing, flexographic printing, newspaper printing, relief printing, letterpress printing, sublimation printing, laser printing, electrophotographic printing processes and combinations of the abovementioned printing processes.

[0052] By applying the coating to that side of the paper substrate on which the preparation is present, the printability of the paper is further improved. Unexpectedly, however, the character of the paper is not changed or not substantially changed by the coating. Both the appearance and the haptic properties of the paper are not adversely influenced or not substantially adversely influenced by the coating. The paper retains the character of an uncoated paper. In comparison with untreated papers, however, the printing quality is significantly improved.

[0053] The present invention is explained below with reference to the following examples, without it being intended to limit it thereto.

10 Examples

1. Preparations

1.1. Production of the preparations 1 to 3

Tylose® H60000 YP2 is dissolved with stirring in the amount of water stated in Table 1 for establishing the desired viscosity. After a clear solution has been obtained, Hydropalat® 120 EXP is added. The corresponding pigment slurry is then added. Stirring is effected for a further 30 minutes in order to obtain the preparations 1 – 3.

Table 1

Ingredients	Preparation 1	Preparation 2	Preparation 3
Tylose® H60000 YP2 <sup>1</sup>	0.1 g	0.1 g	0.1 g
Hydropalat® 120 EXP <sup>2</sup>	0.5 g	0.5 g	0.5 g

Ludox <sup>®</sup> CL <sup>3</sup>	24.6 g		
Cartacoat <sup>®</sup> K 301A liquid <sup>4</sup>		24.6 g	
Ludox <sup>®</sup> TMA <sup>5</sup>			21.8 g
Water	80 g	80 g	80 g

- 1) Tylose<sup>®</sup> H60000 YP2: carboxymethylcellulose having a molecular weight of 60 000 u (Clariant)
- 2) Hydropalat<sup>®</sup> 120 EXP: nonionic surfactant based on EO/PO-modified fatty alcohol, modified fatty alcohol polyglycol ether (Cognis/Henkel)
- 5 3) Ludox<sup>®</sup> CL: cationic colloidal suspension of silica in water (30% by weight of SiO<sub>2</sub>; Grace Davison)
- 4) Cartacoat<sup>®</sup> K 301A liquid: colloidal suspension of nonporous SiO<sub>2</sub> particles (pH 10, 30% of SiO<sub>2</sub>, particle size 12 nm, Clariant)
- 10 5) Ludox<sup>®</sup> TMA: anionic colloidal silica in water (34% by weight of SiO<sub>2</sub>; Grace Davison)

## 1.2. Application of the preparations 1 to 3 to a paper substrate

A paper provided with a neutral size and having a basis weight of  $120 \text{ g/m}^2$  (filler content 15%, filled with PRECARB 200 (Schäfer Kalk), precipitated  $\text{CaCO}_3$ , oil number (measured according to DIN EN ISO 787-5) 65g/100g of powder) is immersed in one of the preparations 1 to 3. The excess amount of preparation is squeezed out between two rubber rolls and the paper is then dried by means of a photodrier (heated metal roll around which a textile web runs; for drying, the paper is introduced into the nip between metal roll and textile web). The coat weight of the preparation on the paper substrate is  $3 \text{ g/m}^2$  (absolutely dry) per side.

## 1.3. Assessment of the printability

The paper substrates provided with the preparations 1 to 3 and, as a comparison, the untreated paper substrate, and a commercially available, coated paper ( $150 \text{ g/m}^2$  total weight, surface-treated,  $20 \text{ g/m}^2$  of a pigment coat are applied to each side of the paper), are printed on one side using a Prüfbau apparatus with a blue printing ink. The homogeneity and intensity of the printed blue area is then visually assessed, the rating 1 denoting very good homogeneity and intensity of the printed blue area and the rating 6 denoting insufficient homogeneity and intensity of the printed blue area. The assessment is shown in Table 2.



Table 2

Sample	Homogeneity and intensity rating
Preparation 1	1-2
Preparation 2	1-2
Preparation 3	1-2
Paper substrate (comparison)	5
Commercially available coated paper (comparison)	1

The commercially available, coated paper received the rating 1 and thus shows very good printability, whereas the paper substrate has only inadequate printability (rating 6). On the other hand, when it was provided with one of the preparations 1 to 3, the paper substrate unexpectedly shows a printability which has the rating 1-2 and is thus only insignificantly poorer than the printability of the coated paper. Nevertheless, the haptic properties and the visual impression of the paper substrate provided with the preparations are not changed or not significantly changed.

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## 2. Coatings

### 2.1. Production of the coatings 1 to 4

Acronal 500D<sup>®</sup> and Mowiol<sup>®</sup> 8/88 solution are added with stirring to the amount of water stated in Table 3. Thereafter, the corresponding pigment slurry and, in the case of the coating 1, additionally Cartacoat<sup>®</sup> MS liquid are added. Stirring is effected for a further 30 minutes in order to obtain the coatings 1 to 4.

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Table 3

Ingredients	Coating 1	Coating 2	Coating 3	Coating 4
Ludox TMA	250 g			
Cartacoat <sup>®</sup> K301A		600 g		
Cartacoat <sup>®</sup> K302C <sup>6</sup>			400 g	
Cartacoat <sup>®</sup> K303A <sup>7</sup>				400 g
Cartacoat <sup>®</sup> MS fl. <sup>8</sup>	0.34 g			
Acronal 500D <sup>®9</sup>	6.8 g	14.4 g	9.6 g	19.2 g
Mowiol <sup>®</sup> 8/88 solution <sup>10</sup>	5.7 g	12.0 g	8.0 g	16.0 g
Water	94.7 g	129.6 g	86.4 g	92.8 g

6) Cartacoat<sup>®</sup> 302C: cationic colloidal suspension of nonporous SiO<sub>2</sub> particles (pH 4, 30% of SiO<sub>2</sub>, particle size 25 nm, Clariant)

5 7) Cartacoat<sup>®</sup> 303A: colloidal suspension of nonporous SiO<sub>2</sub> particles (pH 9, 30% of SiO<sub>2</sub>, particle size 50 nm, Clariant)

8) Cartacoat<sup>®</sup> MS liquid: crosslinked modified polyacrylate (37% solids content)

10 9) Acronal 500D<sup>®</sup>: aqueous dispersion of a polystyrene/vinyl acetate copolymer (50% by weight, BASF AG)

10) Mowiol<sup>®</sup> 8/88 solution: 15% strength polyvinyl alcohol solution, 15% strength solution of Mowiol<sup>®</sup> 8/88 (Clariant) in water.

15 2.2. Application of the coatings 1 to 4 to a paper substrate which was treated with one of the preparations 1 – 3

A paper substrate provided according to 1.2 with one of the preparations 1 to 3 is immersed in one of the coatings 1 to 4. The excess amount of coating is  
20 squeezed out between two rubber rolls, and the paper is then dried by means of a

photodrier (heated metal roll around which a textile web runs; for drying, the paper is introduced into the nip between metal roll and textile web). The coat weight of the coating on the paper substrate provided with the preparation is 3 g/m<sup>2</sup> (absolutely dry) per side.

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### 2.3. Assessment of the printability

The paper substrates provided with the preparations 1 to 4 and, as a comparison, the untreated paper substrate, and a commercially available, coated paper (150 g/m<sup>2</sup> total weight, surface-treated, 20 g/m<sup>2</sup> of a pigment coat are applied to each side of the paper), are printed on one side using a Prüfbau apparatus with a blue printing ink. The homogeneity and intensity of the printed blue area is then visually assessed, the rating 1 denoting very good homogeneity and intensity of the printed blue area and the rating 6 denoting insufficient homogeneity and intensity of the printed blue area. The assessment is shown in Table 4.

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Table 4

Sample		Homogeneity and intensity of the print
Preparation	Coating	Rating
Preparation 1	Coating 1	1
	Coating 2	1
	Coating 3	1
	Coating 4	1
Preparation 2	Coating 1	1
	Coating 2	1
	Coating 3	1
	Coating 4	1
Preparation 3	Coating 1	1
	Coating 2	1
	Coating 3	1
	Coating 4	1
Paper substrate (comparison)		5
Commercially available coated paper (comparison)		1

The commercially available coated paper has the rating 1 and thus shows very good printability, whereas the paper substrate has only inadequate printability (rating 5). On the other hand, when it was provided with one of the preparations 1 to 3 and then with one of the coatings 1 to 4, the paper substrate unexpectedly shows a printability which has the rating 1 and is thus comparable with the printability of the coated paper. Nevertheless, the haptic properties and the visual impression of the paper substrates provided with the preparations and coatings are not changed or not significantly changed.

**Patent claims**

1. Paper comprising:
  - a) a paper substrate and
  - b) a preparation applied to at least one side of the paper substrate over the entire surface and containing at least one surfactant and at least one pigment having a particle diameter of from 1 to 500 nm, but no binder, the preparation containing a binder in a ratio to the pigment of not more than 5 parts by weight of binder : 100 parts by weight of pigment (based in each case on the solids content).
2. Paper according to Claim 1, characterized in that the preparation has a coat weight of from 0.5 to 20 g/m<sup>2</sup> (absolutely dry) per side.
3. Paper according to Claim 1 or 2, characterized in that from 0.05 to 2.5 g/m<sup>2</sup> (absolutely dry) of surfactant are present per side in the preparation.
4. Paper according to any of the preceding claims, characterized in that the surfactant is an anionic, cationic, nonionic or amphoteric surfactant.
5. Paper according to any of Claims 1 to 4, characterized in that from 0.45 to 17.5 g/m<sup>2</sup> (absolutely dry) of pigment are present per side in the preparation.
6. Paper according to any of Claims 1 to 5, characterized in that the pigment has an overall cationic and/or anionic and/or nonionic charge.
7. Paper according to any of Claims 1 to 6, characterized in that the pigment is an oxide and/or mixed oxide of a metal and/or an oxide and/or mixed oxide of a semimetal/semiconductor.



8. Paper according to any of the preceding claims, characterized in that the preparation contains at least one further additive.
9. Paper according to any of Claims 1 to 8, characterized in that the paper substrate contains at least one filler.
- 5 10. Paper according to Claim 9, characterized in that the filler has a cavity volume.
11. Paper according to Claim 9 the 10, characterized in that the filler has an oil number, measured according to DIN EN ISO 787-5, of from 10 to 150 g/ 100 g of filler.
- 10 12. Paper according to any of Claims 9 to 11, characterized in that the filler is selected from the group consisting of chalk, precipitated chalk, clay, talc, calcined clay, alumina, aluminum hydroxide, gypsum, hydrated alumina, silica, silicic acid, diatomaceous earth, titanium dioxide and mixtures thereof.
13. Paper according to any of Claims 1 to 12, characterized in that the paper substrate contains at least one additive.
- 15 14. Paper according to any of the preceding claims, characterized in that at least one further coating is present on the preparation on that side of the paper substrate on which the preparation is applied.
15. Paper according to Claim 14, characterized in that the coating contains at least one pigment and at least one binder.
- 20 16. Paper according to Claim 15, characterized in that the pigment has a particle diameter of from 1 to 500 nm and is preferably selected from the group consisting of oxide and/or mixed oxide of a metal, oxide and/or mixed oxide of a semi-metal/semiconductor and mixtures thereof.

17. Paper according to any of Claims 14 to 16, characterized in that the coating contains at least one further additive.

18. Process for the production of a paper, comprising the step: application of a preparation containing at least one surfactant and at least one pigment having a particle diameter of from 1 to 500 nm to the entire surface on at least one side of a paper substrate, the preparation containing binder in a ratio to pigment of not more than 5 parts by weight of binder : 100 parts by weight of pigment (based in each case on the solids content).

19. Process for the production of a paper according to Claim 18, characterized in that at least one further coating is applied on the preparation on that side of the paper substrate on which the preparation was applied.

20. Use of the paper according to any of Claims 1 to 17 as a print medium in a printing process.

21. Use of the paper according to Claim 20, characterized in that the printing process is selected from the printing processes consisting of offset printing, digital printing, inkjet printing, gravure printing, flexographic printing, newspaper printing, relief printing, letterpress printing, sublimation printing, laser printing, electrophotographic printing processes and combinations of the printing processes.

### **Abstract**

The present invention relates to a paper comprising:

a) a paper substrate and

5       b) a preparation applied to at least one side of the paper substrate over the entire surface and containing at least one surfactant and at least one pigment having a particle diameter of from 1 to 500 nm, the preparation containing a binder in a ratio to the pigment of not more than 5 parts by weight of binder : 100 parts by weight of pigment (based in each case on the solids content),

10       and a process for its production.